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## 14. ABSTRACT

We have used a high-temperature flowing-afterglow Langmuir-probe apparatus to measure rate constants for electron attachment to halomethanes which attach electrons very inefficiently at room temperature, yielding Cl<sup>-</sup> ion product. We studied CH<sub>2</sub>Cl<sub>2</sub> (495-973 K), CF<sub>2</sub>Cl<sub>2</sub> (291-1105 K), and CF<sub>3</sub>Cl (524-1004 K) and include our recent measurement for CH<sub>3</sub>Cl (700-1100 K) in the discussion of the electron attachment results. The measured attachment rate constants show Arrhenius behavior in the temperature ranges examined, from which estimates of rate constants at 300 K may be made: CH<sub>2</sub>Cl<sub>2</sub> (1.8 × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup>), CH<sub>3</sub>Cl (1.1 × 10<sup>-17</sup> cm<sup>3</sup> s<sup>-1</sup>), and CF<sub>3</sub>Cl (4.2 × 10<sup>-14</sup> cm<sup>3</sup> s<sup>-1</sup>), all of which are difficult to measure directly. In the case of CF<sub>2</sub>Cl<sub>2</sub>, the room temperature rate constant was sufficiently large to be measured (1.6 × 10<sup>-9</sup> cm<sup>3</sup> s<sup>-1</sup>). The Arrhenius plots yield activation energies for the attachment reactions: 390 ± 50 meV (CH<sub>2</sub>Cl<sub>2</sub>), 124 ± 20 meV (CF<sub>2</sub>Cl<sub>2</sub>), 670 ± 70 meV (CH<sub>3</sub>Cl), and 406 ± 50 meV (CF<sub>3</sub>Cl). Comparisons are made with existing data where available. G3 calculations were carried out to obtain reaction energetics. They show that the parent anions of CH<sub>2</sub>Cl<sub>2</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, and CF<sub>3</sub>Cl are stable, though CH<sub>3</sub>Cl<sup>-</sup> exists only as an electrostatically bound complex. © 2009 American Institute of Physics. [DOI: 10.1063/1.3212598]

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# Electron attachment to halomethanes at high temperature: CH<sub>2</sub>Cl<sub>2</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, and CF<sub>3</sub>Cl attachment rate constants up to 1100 K

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## I. INTRODUCTION

In a recent publication we described a high-temperature flowing-afterglow Langmuir-probe (HT-FALP) apparatus for use in measuring electron attachment rate constants at temperatures up to 1100 K.<sup>1</sup> We presented data for NF<sub>3</sub> (300–900 K) and CH<sub>3</sub>Cl (600–1100 K).<sup>1</sup> The CH<sub>3</sub>Cl data were found to follow Arrhenius behavior in this temperature range. Extrapolation to room temperature gave a rate constant of  $\sim 10^{-17}$  cm<sup>3</sup> s<sup>−1</sup>. No current apparatus is capable of measuring such a low value, and even if so, the result would be surely dominated by impurities. In the present work, we have made measurements up to 1100 K for other halomethanes which also have very low attachment rate constants at room temperature: CH<sub>2</sub>Cl<sub>2</sub>, CF<sub>3</sub>Cl, and CF<sub>2</sub>Cl<sub>2</sub>. Two of these cases, as with CH<sub>3</sub>Cl, are exothermic toward electron attachment,



The remaining case, of electron attachment to CF<sub>3</sub>Cl, is endothermic



The energies given in Eqs. (1)–(4) are those calculated using the G3 compound method<sup>2</sup> at 0 K, carried out using the GAUSSIAN-03W program.<sup>3</sup> The G3 prescription, which includes empirical corrections based on accurate experimental energies, approximates a quantum configuration interaction calculation with a large basis set. Neutral and anion geometries are optimized at the MP2/6-31G(d) level of theory, and zero-point energies are calculated from scaled Hartree–Fock harmonic frequencies.<sup>2</sup> The G3 method is good, on average, within  $\pm 91$  meV for enthalpies of formation of non-hydrogen-containing molecules and  $\pm 49$  meV for hydrogen-containing molecules.<sup>4</sup> Thus, on the basis of G3 calculations, Eq. (2) cannot be said to be definitely exothermic. However, the quoted exothermicities agree quite well with those derived from tabulated bond dissociation energies (DBEs) and the electron affinity (EA) of Cl, as will be seen later.

G3 calculations (Table I) show that the parent anions exist, and, in fact, CF<sub>3</sub>Cl<sup>−</sup> and CF<sub>2</sub>Cl<sub>2</sub><sup>−</sup> have been observed in electron attachment experiments to CF<sub>3</sub>Cl and CF<sub>2</sub>Cl<sub>2</sub> clusters.<sup>5,6</sup> The parent anions are not observed for electron attachment to the monomers, in beam or thermal experiments, implying that transient parent anions are too short lived even where the gas pressure is high enough that collisional stabilization might occur. Table I includes a comparison of computational and experimental adiabatic EAs where available.<sup>7–9</sup>

## II. EXPERIMENTAL

The HT-FALP apparatus<sup>1,10</sup> has been described previously. The HT-FALP utilizes an electron-He<sup>+</sup>, Ar<sup>+</sup> plasma

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TABLE I. Calculated G3 total energies, adiabatic EAs, and C–Cl BDEs at 0 K for CH<sub>2</sub>Cl<sub>2</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, CF<sub>3</sub>Cl, and dissociation fragments relevant to the energetics of attachment reactions. CHF<sub>3</sub> is included as relevant to comments in the text on endothermic electron attachment to CHF<sub>3</sub>.

Molecule	Total energy (hartree)		EA neutral (eV)	BDE (eV)	
	Neutral	Anion		Neutral <sup>a</sup>	Anion
Parents					
CH <sub>2</sub> Cl <sub>2</sub>	−959.371 21 <sup>b</sup>	−959.394 40	0.631	3.372	0.394
CF <sub>2</sub> Cl <sub>2</sub>	−1157.787 91	−1157.808 56	0.562	3.542	0.495
CH <sub>3</sub> Cl	−499.913 02 <sup>b</sup>	−499.917 68	0.127	3.504	0.023 <sup>c</sup>
CF <sub>3</sub> Cl	−797.546 21	−797.558 14	0.325	3.752	0.467
CHF <sub>3</sub>	−338.086 56 <sup>b</sup>	−337.993 00	−2.546	4.577 <sup>d</sup>	Not stable <sup>e</sup>
Fragments					
CH <sub>2</sub> Cl	−499.256 32	−499.281 86	0.695		
CF <sub>2</sub> Cl	−697.666 78	−697.741 26	2.027		
CH <sub>3</sub>	−39.793 30 <sup>b</sup>	−39.791 85 <sup>b</sup>	−0.039 <sup>f</sup>		
CHF <sub>2</sub>	−238.201 32	−338.228 24	0.733		
CF <sub>3</sub>	−337.417 37	−337.482 98	1.785 <sup>g</sup>		
Cl	−459.990 96 <sup>b</sup>	−460.123 60 <sup>b</sup>	3.609 <sup>h</sup>		

<sup>a</sup>The corresponding experimental values for the neutral molecule C–Cl BDE from Ref. 28 are:  $3.50 \pm 0.03$ ,  $3.46 \pm 0.11$ ,  $3.63 \pm 0.02$ , and  $3.79 \pm 0.04$  eV, respectively.

<sup>b</sup>References 2 and 4.

<sup>c</sup>The calculated C–Cl bond length in CH<sub>3</sub>Cl<sup>−</sup> (3.776 Å), the charge distribution, and the weak BDE implies that the CH<sub>3</sub>–Cl bond in the anion is electrostatic. While the adiabatic EA is low, the vertical EA must be close to EA(Cl).

<sup>d</sup>BDE(CF<sub>3</sub>–H) is listed. BDE(CHF<sub>2</sub>–F) is calculated to be 5.471 eV.

<sup>e</sup>Exothermic toward F<sup>−</sup> loss by 0.476 eV.

<sup>f</sup>Experiment:  $0.08 \pm 0.03$  eV (Ref. 7).

<sup>g</sup>Experiment:  $1.82 \pm 0.05$  eV (Ref. 8).

<sup>h</sup>Experiment:  $3.612\,724 \pm 0.000\,027$  eV (Ref. 9).

moving at high speed in a flow tube reactor entrained in a He buffer gas which contains a few percent Ar. The gas pressure ranged from 1 to 2 Torr. The plasma density decays along the flow tube due to ambipolar diffusion. At a point halfway down the flow tube, an electron-attaching gas is introduced through a four-needle injector. Following this point, the electron density decays because of electron attachment to the reactant gas and diffusion. The decay is monitored along the flow tube axis with a movable Langmuir probe. The ion products of the attachment reaction are sampled at the terminus of the flow tube and mass analyzed. The neutral products are not detected but are usually apparent from the reaction energetics. The plasma velocity is measured in order to provide the time scale for the reaction. Complete data runs for each halomethane were carried out over the available temperature range sequentially, starting with the slowest-attaching gas, to minimize contamination of the feedlines.

The electron attachment frequency  $\nu_a$  is obtained from the equation describing the coupled effects of diffusion and attachment on the electron density,  $n_e(t)$ , as a function of time  $t$  down the flow tube axis,<sup>1,11</sup>

$$n_e(t) = n_e(0)[\nu_a \exp(-\nu_a t) - \nu_D \exp(-\nu_D t)]/(\nu_a - \nu_D). \quad (5)$$

In Eq. (5),  $n_e(0)$  is the electron density at  $t=0$  (at the reactant inlet port),  $\nu_D$  is the diffusion frequency (the ambipolar diffusion coefficient times the square of the characteristic diffusion length for the apparatus), and  $\nu_a$  is the attachment

frequency. The attachment rate constant  $k_a$  is obtained by  $k_a = \nu_a/n_r$ , where  $n_r$  is the reactant concentration in the flow tube. In practice, Eq. (5) is used during data acquisition, and a numerical model that includes possible correction for electron-ion recombination is later fit to the data. A discussion of the rate equations including electron-ion recombination has been given earlier.<sup>1</sup> A recombination correction is only significant when a large concentration of molecular cations is formed from He<sup>+</sup> and Ar<sup>+</sup> reacting with the attaching gas since molecular cations possess large recombination rate constants, typically  $\sim 3 \times 10^{-7}$  cm<sup>3</sup> s<sup>−1</sup> at 300 K, in contrast to the negligible ones for atomic cations. Few molecular cations are usually present in the attachment experiments. Correction becomes noticeable only when  $k_a$  is very small ( $< 5 \times 10^{-10}$  cm<sup>3</sup> s<sup>−1</sup>) because large  $n_r$  is required to achieve a decade of decay of  $n_e(t)$  in the reaction zone. The use of low  $n_e(0)$  mitigates the problem. In the present work, corrections for electron-ion recombination contribution to  $n_e(t)$  decay were as high as 15% at the lowest temperatures for the CF<sub>3</sub>Cl and CH<sub>3</sub>Cl data, but were only 2% at 900 K because the attachment rate constants were larger and the estimated ion molecule and recombination rates were lower.<sup>1</sup> We will assign a larger uncertainty to results for which appreciable recombination correction was required. The numerical model also accounts for ion-ion mutual neutralization, though an indiscernible effect for the  $n_e(0)$  used in the present work. Rate constants for Ar<sup>+</sup>+CH<sub>2</sub>Cl<sub>2</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, and CF<sub>3</sub>Cl were measured at 300 K by Smith *et al.*<sup>11</sup> and assumed in the

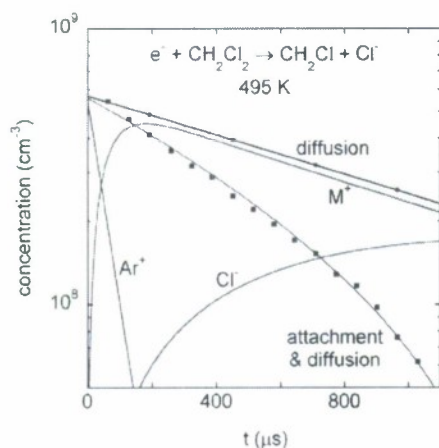


FIG. 1. Data obtained with the HT-FALP apparatus for  $\text{CH}_2\text{Cl}_2$  ( $9.5 \times 10^{12} \text{ cm}^{-3}$ ) at 495 K in a He/Ar buffer gas ( $3.1 \times 10^{16} \text{ cm}^{-3}$ ) vs reaction time  $t$ . The diffusion data ( $v_D = 818 \text{ s}^{-1}$ ) were obtained in the absence of the  $\text{CH}_2\text{Cl}_2$ . The solid curves are solutions of rate equations using  $k_a = 6.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .  $\text{M}^+$  represents molecular cations produced in reaction with  $\text{Ar}^+$  (and some  $\text{He}^+$ ). The  $\text{Ar}^+ + \text{CH}_2\text{Cl}_2$  reaction rate was taken to be  $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , and the electron recombination rate constant was estimated at  $2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 495 K.

present work to decrease with temperature according to the trajectory calculations of Su and Chesnavich.<sup>12</sup> The electron recombination rate constant was estimated at  $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  ( $300/T$ )<sup>1/2</sup> in all cases.<sup>13</sup>

Figure 1 gives an example of data obtained with the HT-FALP apparatus for  $\text{CH}_2\text{Cl}_2$  at 495 K, where  $k_a$  is small enough that a large concentration of  $\text{CH}_2\text{Cl}_2$  is needed. Note the rapid increase in production of molecular cations ( $\text{M}^+$  in Fig. 1) due to the reaction between  $\text{Ar}^+$  and  $\text{CH}_2\text{Cl}_2$ . The electron-ion correction in that case was held to an acceptable value, 14%, through the use of a low value of  $n_e(0) = 5.7 \times 10^8 \text{ cm}^{-3}$ . The disadvantage of low  $n_e(0)$  is that long reaction times correspond to low electron concentrations, which are more difficult to measure accurately with the Langmuir probe.

The estimated uncertainty in the data is  $\pm 25\%$  except

for cases where significant correction is required for electron-ion recombination. If  $k_a < 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , then the estimated uncertainty is  $\pm 35\%$ .

### III. RESULTS AND DISCUSSION

Table II lists the present attachment data for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CF}_3\text{Cl}$ . Figure 2 shows these data plotted in Arrhenius form in comparison with literature data from Birmingham University,<sup>11</sup> Oak Ridge National Laboratory (ORNL),<sup>14,15</sup> and Boston College.<sup>16</sup> Outside the temperature scale of Fig. 2 are data for  $\text{CF}_2\text{Cl}_2$  obtained at temperatures of 75–170 K at the University of Rennes using a low temperature nozzle jet, which show the breakdown of Arrhenius behavior at low temperatures.<sup>17</sup> The Birmingham University FALP data<sup>11</sup> for  $\text{CF}_2\text{Cl}_2$  (295–590 K) lie above those of Boston College<sup>16</sup> (293–777 K) and the present data (291–1105 K), but the Arrhenius activation energies are in rough agreement (150, 127, and 124 meV, respectively). A complete review and critical examination of data for attachment to  $\text{CF}_2\text{Cl}_2$ , including beam experiments, has been given by Skalny *et al.*<sup>18</sup> and Christophorou and Olthoff.<sup>19</sup>

Figure 2 and Table II include results for  $\text{CH}_2\text{Cl}_2$  that we deduced from drift tube data of the ORNL group.<sup>14</sup> The deduced thermal  $k_a$  merge well with the present results at higher temperature, and the Arrhenius slopes agree well (378 meV, ORNL data, and 390 meV, present data) for  $\text{CH}_2\text{Cl}_2$ . The Boston College data show a lower Arrhenius slope of 248 meV.<sup>16</sup> The  $\text{CF}_3\text{Cl}$  data in Fig. 2 likewise give a lower slope for Boston College data<sup>16</sup> (316 meV) than found in the present work (406 meV).

Figure 3 shows temperature dependences for the fluorine- and chlorine-containing halomethanes along with our earlier  $\text{CH}_3\text{Cl}$  data<sup>1</sup> and some data from other sources.<sup>11,14,20</sup> It was not possible to fit all literature data clearly on this one figure. Shown are the present data for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CF}_3\text{Cl}$ , our recently published data for  $\text{CH}_3\text{Cl}$ ,<sup>1</sup> ORNL data for  $\text{CH}_2\text{Cl}_2$ ,<sup>14</sup> temperature-dependent data for  $\text{CCl}_4$ ,  $\text{CFCl}_3$ , and  $\text{CHCl}_3$  from Birmingham

TABLE II. Electron attachment rate constants  $k_a$  for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CF}_3\text{Cl}$  obtained at temperatures  $T$ . Data for  $\text{CH}_3\text{Cl}$  were given in Ref. 1. The present experimental uncertainty is  $\pm 25\%$  except for cases where significant correction for electron-ion recombination was made: If  $k_a < 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , then the estimated uncertainty is  $\pm 35\%$ .

$T$ (K)	$\text{CH}_2\text{Cl}_2$ <sup>a</sup> $k_a$ ( $\text{cm}^3 \text{ s}^{-1}$ )	$T$ (K)	$\text{CF}_2\text{Cl}_2$ $k_a$ ( $\text{cm}^3 \text{ s}^{-1}$ )	$T$ (K)	$\text{CF}_3\text{Cl}$ <sup>b</sup> $k_a$ ( $\text{cm}^3 \text{ s}^{-1}$ )
300 <sup>c</sup>	$2.6 \times 10^{-13}$	291	$1.6 \times 10^{-9}$	524	$3.1 \times 10^{-11}$
400 <sup>c</sup>	$7.0 \times 10^{-12}$	352	$3.4 \times 10^{-9}$	654	$2.6 \times 10^{-10}$
500 <sup>c</sup>	$9.5 \times 10^{-11}$	400	$6.0 \times 10^{-9}$	800	$8.2 \times 10^{-10}$
495	$7.0 \times 10^{-11}$	500	$1.1 \times 10^{-8}$	898	$1.3 \times 10^{-9}$
591	$3.1 \times 10^{-10}$	525	$1.4 \times 10^{-8}$	1004	$2.5 \times 10^{-9}$
684	$8.2 \times 10^{-10}$	652	$2.0 \times 10^{-8}$		
790	$2.0 \times 10^{-9}$	801	$3.5 \times 10^{-8}$		
892	$4.6 \times 10^{-9}$	900	$4.5 \times 10^{-8}$		
973	$5.5 \times 10^{-9}$	1004	$6.3 \times 10^{-8}$		
		1105	$6.1 \times 10^{-8}$		

<sup>a</sup>The present data extrapolated to 300 K imply  $k_a = 1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

<sup>b</sup>The present data extrapolated to 300 K imply  $k_a = 4.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ .

<sup>c</sup>ORNL data (Ref. 14) extrapolated to thermal energies.



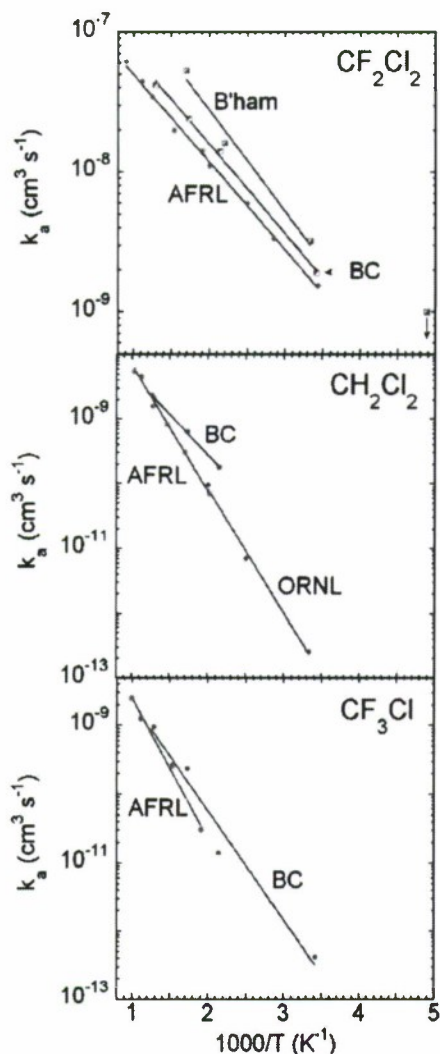


FIG. 2. Comparison of the present data (AFRL) with those of Boston College (BC, Ref. 16), Birmingham University (B'ham, Ref. 11), and Oak Ridge National Laboratory (ORNL, Ref. 14, extrapolated to thermal energy in the present work). Off scale are Rennes data (Ref. 16) at temperatures of <170 K.

University,<sup>11</sup> and a number of 300 K measurements from ORNL.<sup>20</sup> In an earlier work, we gave comparisons for attachment to  $\text{CH}_3\text{Cl}$ , for which we found an Arrhenius slope of  $670 \pm 70$  meV.<sup>1</sup> The only other data at high temperatures for  $\text{CH}_3\text{Cl}$  are unpublished data from Boston College<sup>21</sup> (932 and 1022 K), which agree quite well with the AFRL data. Fabrikant<sup>22</sup> carried out *R*-matrix calculations of dissociative attachment cross sections for  $\text{CH}_3\text{Cl}$  for temperatures of 200–800 K, with absolute magnitudes pinned to experimental vibrational excitation cross sections. Rate constants were given in a later work.<sup>23</sup> We had to multiply the calculated rate constants by a factor of 8 to have them merge with our measurements of  $k_a$ , but the Arrhenius slopes were in acceptable agreement [611 meV (calculated) and 670 meV (experiment)].

There are four main points to be made from Fig. 3.

- (a) The halomethane data in Fig. 3 cover seven orders of magnitude in attachment rate constant.

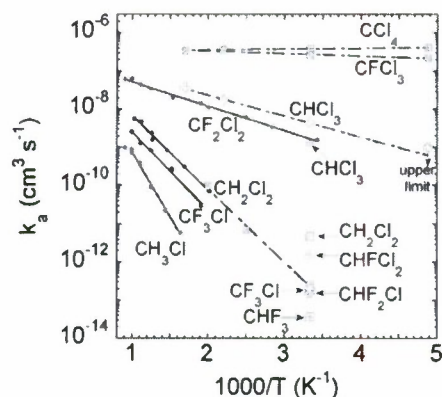


FIG. 3. Temperature dependence of halomethane electron attachment rate constants. Solid circles are the present (AFRL) data. The other data showing temperature dependences are those of Birmingham University (Ref. 11), except for  $\text{CH}_2\text{Cl}_2$  (at 300, 400, and 500 K) which are from ORNL (Ref. 14). The points shown only at 300 K are all ORNL data (Ref. 20). The  $\text{CHF}_3$  datum is likely in error (see text).

- (b) The temperature dependences all seem to be pointing toward a collisional rate constant (at infinite temperature) in the neighborhood of  $4 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ . Even if the extrapolations were accurate, the collisional rate constant will not be the same for all of these molecules because of their differing polarizabilities and dipole moments.
- (c) The ORNL 300 K data and the general Arrhenius picture formed from temperature-dependent data in Fig. 3 allow one to make an educated guess as to the temperature dependence for attachment to these other compounds. Generally speaking, the lower the rate constant lies at 300 K, the greater will be the temperature dependence, as if pointing toward a collisional rate constant at infinite temperature. However, we assume that the ORNL result<sup>24</sup> and the one of Fessenden and Bansal<sup>25</sup> for the slowest-attaching halomethane shown,  $\text{CHF}_3$ , is in error because dissociative electron attachment is 2 eV endothermic, and there is no evidence for a stable parent anion.  $\text{CHF}_3$  has a negative EA,  $-2.55$  eV (G3 calculation, Table 1), consistent with the fact that no parent anion has been observed. Wang *et al.*<sup>26</sup> found a  $k_a$  value of  $1.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  but noted that the reaction was probably endothermic and concluded that attachment to  $\text{CHF}_3$  “is very weak or absent” at thermal energy. Jarvis *et al.*<sup>27</sup> reported no measurable electron attachment to  $\text{CHF}_3$  within the sensitivity of their instrument (about  $2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ). The  $\text{CHF}_3$  data reinforce a point made earlier that extremely small  $k_a$  is difficult to measure because the slightest impurity may dominate. With three of the halomethanes we have studied,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CF}_3\text{Cl}$ , we did not measure the rate constants below 500 or 600 K because of the difficulty of measuring small  $k_a$ .
- (d) Replacing Cl atoms by either H or F atom reduces  $k_a$ , but replacement with an F atom is much less dramatic. Starting with  $\text{CCl}_4$ , replacement with a single F barely changes  $k_a$ , but replacement with a single H changes  $k_a$  by two orders of magnitude. A second Cl replacement

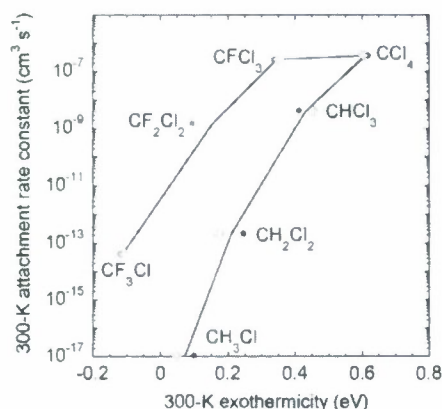


FIG. 4. Correlation of 300 K electron attachment rate constants (yielding  $\text{Cl}^-$  ion product) with reaction exothermicity (a negative value implying endothermicity). The lines are drawn to guide the eyes for molecules containing no F atoms (right) and molecules with no H atoms (left). The closed circles are data plotted vs energetics from G3 calculations (Table I). The open points are the same data plotted vs energetics deduced from BDEs minus  $E_A(\text{Cl})$ .

with an F atom changes  $k_a$  by a larger amount and makes the reaction nearly thermoneutral. Replacement of Cl with a second H atom has a much greater effect in reducing  $k_a$ . The importance of the Cl atoms has, of course, been noted before (see Refs. 20 and 27).

These statements are illustrated in Fig. 4. The reaction energies at 298 K used in Fig. 4 were obtained (a) from G3 calculations and (b) from 298 K BDEs listed in the *Handbook of Chemistry and Physics*,<sup>28</sup> subtracted from the EA of Cl (unchanged between 0 and 298 K).<sup>9</sup> The two methods agree well except for a 0.12 eV discrepancy for the  $\text{CF}_2\text{Cl}_2$  case. However, the BDE in that case is tabulated as uncertain to  $\pm 0.09$  eV, and the G3 calculations have a similar uncertainty.

The Arrhenius plots of the present data may be used to predict 300 K values of  $k_a$  for these compounds:  $\text{CH}_2\text{Cl}_2$  ( $1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ),  $\text{CH}_3\text{Cl}$  ( $1.1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ), and  $\text{CF}_3\text{Cl}$  ( $4.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ). The extrapolated value for  $\text{CH}_2\text{Cl}_2$  may be compared to the 300 K estimate of  $2.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  from our analysis of ORNL drift tube data.<sup>14</sup> Considering uncertainties in both sets of data and extrapolations, the agreement is reasonable if not surprisingly so. However, three older measurements for  $\text{CH}_2\text{Cl}_2$  are tabulated by Christophorou *et al.*<sup>20</sup> which tend to cluster around a value 20 times larger, at  $4.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K. For  $\text{CH}_3\text{Cl}$ , only upper limits are tabulated by Christophorou *et al.*<sup>20</sup> at 300 K, and all are consistent with the present work. For  $\text{CF}_3\text{Cl}$ , Christophorou *et al.*<sup>20</sup> tabulated four older measurements, all lying higher than the present estimate of  $k_a$  at 300 K, but not unreasonably so ( $5.2 \times 10^{-14}$ ,  $7 \times 10^{-14}$ , and  $20 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ). In the case of  $\text{CF}_2\text{Cl}_2$ , we were able to make a measurement at room temperature, obtaining  $k_a = 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . Christophorou and Olthoff<sup>19</sup> tabulated measured values of  $k_a$  for  $\text{CF}_2\text{Cl}_2$  with a mean value of  $1.57 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 293–300 K. The Birmingham group measured  $3.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{CF}_2\text{Cl}_2$  at 300 K.<sup>11</sup> Their results for 205–590 K are shown in Fig. 3.

The negative of the slopes<sup>29</sup> of the Arrhenius plots (multiplied by Boltzmann's constant) are used as the activation energy needed to overcome endothermicity or to surmount a barrier if the reaction is exothermic. Fabrikant and Hotop<sup>30</sup> gave an analysis of Arrhenius plots for dissociative electron attachment. For our sole endothermic case, that of  $\text{CF}_3\text{Cl}$ , their analysis indicates that the Arrhenius activation energy should be close to the threshold energy. The Arrhenius plot shown in Fig. 2 yields an activation energy of  $406 \pm 50 \text{ meV}$ . The calculated endothermicity of the reaction is only 143 meV at 298 K (118 meV at 298 K), so there is apparently a barrier to attachment beyond simply the endothermicity. The barrier is likely related to the crossing point of the anion potential surface, requiring vibrational energy input to  $\text{CF}_3\text{Cl}$  in order to access the anion surface efficiently.<sup>30</sup>

Relevant to the exothermic  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CF}_2\text{Cl}_2$  reactions, the Fabrikant–Hotop analysis says that the Arrhenius activation energy is lower than the barrier height, but comes closer to the barrier height if the vibrational frequency of the molecule most active in dissociation is a low frequency.<sup>30</sup> The Arrhenius activation energies are  $390 \pm 50 \text{ meV}$  ( $\text{CH}_2\text{Cl}_2$ ),  $670 \pm 70 \text{ meV}$  ( $\text{CH}_3\text{Cl}$ ), and  $126 \pm 20 \text{ meV}$  ( $\text{CF}_2\text{Cl}_2$ ). The C–Cl stretching frequencies are in the neighborhood of  $700 \text{ cm}^{-1}$  (87 meV), a value which is not “small” in the Fabrikant–Hotop analysis.<sup>30</sup> Thus, the anion potential surface for the three exothermic cases studied here would seem to be crossing the neutral surface at a point well above the energies given by the Arrhenius slopes. Calculation of the neutral and anion potential curves along a C–Cl bond for these molecules would be useful in understanding the measured activation energies.

We note that many other measurements have been made of the activation energy in the  $\text{CF}_2\text{Cl}_2$  attachment reaction. In electron beam experiments, the activation energy has been obtained from the growth with temperature of the zero-energy resonance. Hahndorf and Illenberger<sup>31</sup> studied the temperature dependence of attachment to several halomethanes, including  $\text{CF}_3\text{Cl}$  (no observable zero-energy resonance) and  $\text{CF}_2\text{Cl}_2$ , between 350 and 700 K. Skalny *et al.*<sup>18</sup> analyzed many different results for  $\text{CF}_2\text{Cl}_2$  obtained in beam, electron swarm, and true thermal experiments to reconcile the results from the very different experiments. They compiled  $k_a$  values ranging from 75 to 777 K. The lowest-temperature data (75–171 K) are from the Rennes group,<sup>17</sup> and the highest-temperature data included (293–777 K) are from the Boston College group.<sup>16</sup> The Arrhenius plot containing all of these data shows Arrhenius behavior for temperatures greater than 150 K. Values of  $k_a$  below this temperature (from Rennes)<sup>17</sup> show much less variation with temperature, which may be a result of population of only the lowest vibrational levels. Skalny *et al.* pointed out that while there is considerable difference in the activation energies determined from all of the experiments (73–195 meV), it is clear that activation energies from electron beam experiments ( $\sim 85 \text{ meV}$ ) are lower than those from swarm and thermal experiments ( $\sim 150 \text{ meV}$ ).<sup>18</sup>

Dashevskaya *et al.*<sup>32</sup> gave a formula for the collisional electron attachment rate constant which serves to evaluate



the efficiency of the measured reactions. Using tabulated polarizabilities<sup>33</sup> and dipole moments,<sup>34</sup> the formula of Dashkevskaya *et al.* gives  $k_a = 3.81$  ( $\text{CH}_2\text{Cl}_2$ ), 3.02 ( $\text{CF}_2\text{Cl}_2$ ), 4.06 ( $\text{CH}_3\text{Cl}$ ), and 2.78 ( $\text{CF}_3\text{Cl}$ ) at 300 K, in units of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ . Attachment to all of these molecules is inefficient at 300 K, with  $\text{CH}_3\text{Cl}$  attaching electrons in only one of every  $3.7 \times 10^{10}$  collisions at 300 K.

#### IV. CONCLUSIONS

We have measured electron attachment rate constants for  $\text{CH}_2\text{Cl}_2$  (495–973 K),  $\text{CF}_2\text{Cl}_2$  (291–1105 K),  $\text{CH}_3\text{Cl}$  (700–1100 K), and  $\text{CF}_3\text{Cl}$  (524–1004 K) using a HT-FALP apparatus. The results display Arrhenius behavior in the studied temperature ranges and allow estimates of extremely small rate constants at 300 K to be made. The activation energies range from 124 meV ( $\text{CF}_2\text{Cl}_2$ ) to 670 meV ( $\text{CH}_3\text{Cl}$ ). The  $\text{CH}_2\text{Cl}_2$  results merge well with rate constants measured at lower temperatures by the ORNL group, extrapolated to thermal energies.<sup>14</sup> Arrhenius plots of the present data, taken together with attachment rate constants measured at 300 K by others (which cover seven orders of magnitude), allow one to estimate the high-temperature behavior for several other halomethanes. The attachment rate constants show a strong dependence on reaction exothermicity. G3 calculations were carried out, showing that the parent anions of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CF}_3\text{Cl}$  are stable, though  $\text{CH}_3\text{Cl}^-$  exists only as an electrostatically bound complex. However, the parent anions are not observed in attachment experiments to the monomer neutrals. G3 calculations imply that  $\text{CHF}_3$  should not undergo an electron attachment reaction at all, whether dissociatively or nondissociatively. Literature studies for  $\text{CHF}_3$  underscore a point that extremely small attachment rate constants are difficult to measure because of interference from even trace impurities.

*Note added in proof:* Recent experiments with high electron energy resolution have been carried out by K. Graupner, S. A. Haughey, T. A. Field, C. A. Mayhew, T. H. Hoffmann, O. May, J. Fedor, M. Allan, I. I. Fabrikant, E. Illenberger, M. Braun, M.-W. Ruf, and H. Hotop (to be published) which show cusp structures in the electron attachment cross section for  $\text{CF}_2\text{Cl}_2$  at thresholds for vibrational excitation of the  $\nu_3(a_1)$  mode due to interaction between attachment and vibrational excitation channels, among other results.

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<sup>1</sup>T. M. Miller, J. F. Friedman, J. S. Williamson, L. C. Schaffer, and A. A. Viggiano, *Rev. Sci. Instrum.* **80**, 034104 (2009).

<sup>2</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7754 (1998).

<sup>3</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN-03W, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

<sup>4</sup>L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **123**, 124107 (2005).

<sup>5</sup>A. Kühn and E. Illenberger, *J. Phys. Chem.* **93**, 7060 (1989).

<sup>6</sup>J. Langer, S. Mott, M. Meinke, P. Tegeder, A. Stamatovic, and E. Illenberger, *J. Chem. Phys.* **113**, 11063 (2000).

<sup>7</sup>G. B. Ellison, P. C. Engelking, and W. C. Lineberger, *J. Am. Chem. Soc.* **100**, 2556 (1978).

<sup>8</sup>H.-J. Deyerl, L. S. Alconcel, and R. E. Continetti, *J. Phys. Chem. A* **105**, 552 (2001).

<sup>9</sup>C. Blondel, C. Delsart, and F. Goldfarb, *J. Phys. B* **34**, L281 (2001).

<sup>10</sup>J. F. Friedman, T. M. Miller, L. C. Schaffer, A. A. Viggiano, and I. I. Fabrikant, *Phys. Rev. A* **79**, 032707 (2009).

<sup>11</sup>D. Smith, N. G. Adams, and E. Alge, *J. Phys. B* **17**, 461 (1984).

<sup>12</sup>T. Su and W. J. Chesnavich, *J. Chem. Phys.* **76**, 5183 (1982); T. Su, *ibid.* **89**, 5355 (1988); **88**, 4102 (1988). We used the parametrized formula given in the final citation, except that the dimensionless temperature  $T_R$  is misprinted:  $T_R = 2\alpha k_B T / \mu_D^2$ .

<sup>13</sup>M. Larsson and A. E. Orel, *Dissociative Recombination of Molecular Ions* (Cambridge University Press, Cambridge, 2008), pp. 267–271. The correction of the present data for electron-ion recombination events used a rough average of rate constants for polyatomic ions.

<sup>14</sup>L. A. Pinnaduwa, C. Tav, D. L. McCorkle, and W. X. Ding, *J. Chem. Phys.* **110**, 9011 (1999). These  $\text{CH}_2\text{Cl}_2$  data (300, 400, and 500 K) did not extend quite to thermal electron energies. However, we found that the low-energy rate constant data at 400 and 500 K could be fitted quite precisely to a power law in mean electron energy and then extrapolated to thermal energy with confidence. The 300 K rate constants could be similarly well fit provided that the three lowest-energy data were ignored. Our fits, with  $\epsilon$  as the mean thermal electron energy in eV, are  $3.916 \times 10^{-10} \times \epsilon^{2.2549} \text{ cm}^3 \text{ s}^{-1}$  (300 K),  $9.245 \times 10^{-10} \times \epsilon^{1.6461} \text{ cm}^3 \text{ s}^{-1}$  (400 K), and  $1.3175 \times 10^{-9} \times \epsilon^{0.95811} \text{ cm}^3 \text{ s}^{-1}$  (500 K).

<sup>15</sup>D. L. McCorkle, A. A. Christodoulides, L. G. Christophorou, and I. Szamrej, *J. Chem. Phys.* **72**, 4049 (1980); **76**, 753 (1982).

<sup>16</sup>S. J. Burns, J. M. Matthews, and D. L. McFadden, *J. Phys. Chem.* **100**, 19436 (1996).

<sup>17</sup>J. L. Le Garrec, O. Sidko, J. L. Queffelec, S. Hamon, J. B. A. Mitchell, and B. R. Rowe, *J. Chem. Phys.* **107**, 54 (1997).

<sup>18</sup>J. D. Skalny, S. Matejcek, T. Mikoviny, and T. D. Märk, *Int. J. Mass Spectrom.* **223–224**, 217 (2003).

<sup>19</sup>L. G. Christophorou and J. K. Olthoff, *Fundamental Electron Interactions with Plasma Processing Gases* (Kluwer Academic, New York/Plenum, New York, 2004), pp. 553–554.

<sup>20</sup>L. G. Christophorou, D. L. McCorkle, and A. A. Christodoulides, in *Electron-Molecule Interactions and Their Applications*, edited by L. G. Christophorou (Academic, New York, 1984), Vol. 1, Chap. 6.

<sup>21</sup>A preliminary description of the Boston College experiments, in an apparatus capable of reaching 1200 K, was given by D. L. McFadden, "Chemical kinetics and atmospheric modification," Final Report No. PL-TR-94-2164, 1994, available online from the Defense Technical Information Center at <http://handle.dtic.mil/100.2/ADA283304>.

<sup>22</sup>I. I. Fabrikant, *J. Phys. B* **27**, 4325 (1994).

<sup>23</sup>R. S. Wilde, G. A. Gallup, and I. I. Fabrikant, *J. Phys. B* **33**, 5479 (2000).

<sup>24</sup>A. A. Christodoulides, R. Schumacher, and R. N. Schindler, *Int. J. Chem. Kinet.* **10**, 1215 (1978).

<sup>25</sup>R. W. Fessenden and K. M. Bansal, *J. Chem. Phys.* **53**, 3468 (1970).

<sup>26</sup>Y. Wang, L. G. Christophorou, J. K. Olthoff, and J. K. Verbrugge, *Chem. Phys. Lett.* **304**, 303 (1999).

<sup>27</sup>G. K. Jarvis, C. A. Mayhew, L. Singleton, and S. M. Spyrou, *Int. J. Mass Spectrom. Ion Process.* **164**, 207 (1997).

<sup>28</sup>Y.-R. Luo, in *Handbook of Chemistry and Physics*, 88th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 2008), pp. 56–80.

<sup>29</sup>The Arrhenius fits in Fig. 2 are as follows:  $\text{CH}_2\text{Cl}_2$ ,  $6.4226 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \exp[-390.1/kT \text{ (meV)}]$ , and the fit to our deduced  $k_a$  from ORNL data is  $5.2896 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \exp[-378.2/kT \text{ (meV)}]$ ;  $\text{CH}_3\text{Cl}$ ,  $1.6816 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \exp[-665.9/kT \text{ (meV)}]$ ;  $\text{CF}_3\text{Cl}$ ,  $2.8224 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \exp[-406.4/kT \text{ (meV)}]$ ; and  $\text{CF}_2\text{Cl}_2$ ,  $2.2006 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \exp[-125.9/kT \text{ (meV)}]$ .

<sup>30</sup>I. I. Fabrikant and H. Hotop, *J. Chem. Phys.* **128**, 124308 (2008).

<sup>31</sup>I. Hahndorf and E. Illenberger, *Int. J. Mass Spectrom.* **167/168**, 87 (1997).

<sup>32</sup>E. I. Dashkevskaya, I. Litvin, E. E. Nikitin, and J. Troe, *Phys. Chem. Chem. Phys.* **10**, 1270 (2008).

<sup>33</sup>T. M. Miller, in *Handbook of Chemistry and Physics*, 88th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 2008), Sec. 10, pp. 193–202. The polarizabilities are  $7.2 \text{ \AA}^3$  ( $\text{CH}_2\text{Cl}_2$ ),  $7.93 \text{ \AA}^3$  ( $\text{CF}_2\text{Cl}_2$ ),  $5.35 \text{ \AA}^3$  ( $\text{CH}_3\text{Cl}$ ), and  $5.72 \text{ \AA}^3$  ( $\text{CF}_3\text{Cl}$ ).

<sup>34</sup>*Handbook of Chemistry and Physics*, 88th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 2008), Sec. 9, pp. 47–55. The dipole moments are  $1.60 \pm 0.03 \text{ D}$  ( $\text{CH}_2\text{Cl}_2$ ),  $0.51 \pm 0.05 \text{ D}$  ( $\text{CF}_2\text{Cl}_2$ ),  $1.8963 \pm 0.0002 \text{ D}$  ( $\text{CH}_3\text{Cl}$ ), and  $0.50 \pm 0.01 \text{ D}$  ( $\text{CF}_3\text{Cl}$ ).